Magnetic properties of superconducting niobium near T_c

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A vibration magnetometer was used to measure the magnetization curves of pure ($\rho_{300K}/\rho_{10K} = 840$) niobium. It is shown that absolutely pure niobium is a type-II superconductor with $\varkappa_0 \approx 0.746$–$0.738$. The temperature dependence of the equilibrium induction B_0 and the value of the first critical field H_{c1} agree with the theoretical values, and the parameters $\varkappa_1$ and $\varkappa_2$ increase much more strongly than predicted by the theory when the temperature is lowered from T_c.

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1. INTRODUCTION

As shown in a number of theoretical and experimental studies,[1-5] a first-order phase transition takes place from the Meissner state into the mixed state with equilibrium induction B_0 takes place in pure (electron mean free path l much larger than the coherence length ξ_0) type-II superconductors with small values of the Ginzburg-Landau parameter $\varkappa_0$, in magnetic field values equal to the first critical H_{c1}. The presence of a finite induction B_0 is the result of the presence in the free energy of a mixed term corresponding to the "condensation energy."[3] This term ensures attraction of the fluxoids in the nonlocal approximation at small $\varkappa_0$. In addition, at temperatures not too close to T_c the presence of oscillations in the coordinate dependence of the magnetic field of an individual fluxoid may come into play[4] and lead to a nonmonotonic dependence of the fluxoid interaction energy on the distance between them.

A theoretical calculation of the temperature dependence of the initial induction B_0 (Ref. 5) shows that at $\varkappa_0 > 2^{-1/2}$ the ratio B_0/H_{c2} has a maximum at $t = T/T_c \approx 0.7$ and decreases to zero in a narrow temperature range near $t = 1$; this agrees with the results of the Ginzburg-Landau theory, which is valid when $t \to 1$. At $\varkappa_0 = 2^{-1/2}$ the ratio B_0/H_{c2} increases with temperature and at $t = 1$ we have $B_0 = H_{cm}$.

One of the small-$\varkappa_0$ superconductors most thoroughly investigated experimentally is niobium. At temperatures not too close to T_c, many workers have determined its properties reliably enough (see the literature cited in Refs. 6 and 7) and have demonstrated that a first-order phase transition takes place in H_{c1}. Near T_c, however, the situation with niobium is contradictory. What remains in fact unanswered is whether the basic parameter $\varkappa_0$ is larger or smaller than $2^{-1/2}$, i.e., it is not clear whether niobium is a type-I or type-II superconductor. It was found in Ref. 6 that sufficiently pure ($\rho_{300K}/\rho_{res} \geq 3000$) niobium has $\varkappa_0 < 2^{-1/2}$, but determination of B_0 from the magnetization curves[7] shows no increase of B_0/H_{c2} as $t \to 1$, but a tendency of this quantity to decrease.

In practically all the reported measurements of the magnetization curves of niobium they used an integrating method[6,7] which calls for a rather fast sweep of the magnetic field to increase the signal/noise ratio. In the presence of dynamic effects that frequently accompany first-order transitions, this method does not always yield the equilibrium magnetization curve. In addition, the integrating method is found to be not sensitive enough in the immediate vicinity of T_c.

To determine the magnetic properties of niobium near T_c, we have measured the magnetization curves of sufficiently pure ($l/\xi_0 \approx 100$) material with a vibration magnetometer whose sensitivity is high enough[8] and does not depend on the field sweep rate.

2. MEASUREMENT PROCEDURE AND REDUCTION OF THE EXPERIMENTAL DATA

The magnetization curves were plotted with a vibration magnetometer having provisions for changing and stabilizing the temperature. The sample was located at the center of a superconducting solenoid compensated up to sixth order. The temperature sensor was an Allen-Bradley resistor calibrated at three points—the boiling temperature of liquid helium and the superconducting transition points of high-purity lead and niobium. The temperature stability in the measurements was 0.005 K/h.

The single crystal was obtained by electron-beam crucibleless zone melting in a vacuum of 2×10^{-5} Torr (two forming passes at 5 mm/min and on growth pass at 1 mm/min). A sphere of 9.5 mm diameter was cut out of the single-crystal rod with a lathe. After polishing with fine abrasive pastes and bright-dipping in a mixture of equal parts of HNO_3 and HF, the final sphere diameter was 8.9 mm, and the deviation for sphericity did not exceed ±0.1 mm. The sample was annealed in a vacuum of 1×10^{-9} Torr at a temperature 2570 K for five hours. The sample resistivity ratio measured after plotting all the magnetization curves was $\rho_{300K}/\rho_{10K} \approx 840$. An estimate of the quantity $\xi_0/\langle l\rangle$, which characterizes the purity of the investigated sample, was based on the formula

$$\xi_0/\langle l\rangle = 0.18\rho_{res}e^2h\gamma\langle v_F^2\rangle/2\pi^3k^3T_c, \tag{1}$$

obtained from the known[9] expressions for $\langle l\rangle$ and ξ_0. It was assumed that $T_c = 9.25$ K, $\gamma = 7.2\times10^3$ erg/cm$^3\cdot$K^2, and $\rho_{res} = 1.67\times10^{-8}\ \Omega\cdot$cm $= \rho_{10K}$.

The electron velocity averaged over the Fermi surface was estimated from the relation (see, e.g., Ref. 6)

$$\langle v_F^2\rangle = -\frac{6c(2\pi kT_c)^2}{7\zeta(3)eh(dH_{c2}/dt)_{t=1}}. \tag{2}$$

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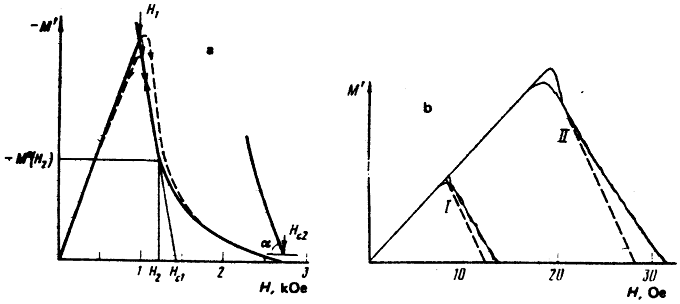

FIG. 1. Magnetization curves of niobium: 1) $T=4.2$ K, dashed line—after high-vacuum annealing, solid—after oxidation. The section near H_{c2} is plotted with tenfold magnification. b) Near T_c: I—$t=0.997$; II—$t=0.993$. The absolute values of the magnetic field were not measured.

In our case $(dH_{c2}/dt)_{t=1}=4340$ Oe and $\xi_0/\langle l\rangle \approx 1.4\times 10^{-2} \ll 1$, i.e., as regards its superconducting properties the sample employed should be considered to be at the purity limit.

Immediately after annealing, without breaking the vacuum, the sample was cooled to $T\approx 95$ K and was mounted cooled in the magnetometer. The sample magnetization curves without heating and after subsequent heating to room temperature did not differ from one another and revealed appreciable hysteresis near H_1 (Fig. 1a). We note that the magnetization curves have linear sections in both increasing and decreasing fields, but the magnetization factor determined from the averaged values of $M(H)$ in this region is undervalued.

To remove the surface barrier and obtain a more reversible magnetization curve we use the standard procedure: the sample was heated at 670 K for five minutes in an oxygen atmosphere. The resultant magnetization curve is also shown in Fig. 1a. The irreversibility of the curve was indeed reduced. The demagnetization factor determined from the ratio of the slopes of the linear sections of the magnetization curve (in the field ranges $0-H_1$ and H_1-H_2 is $n\approx 0.336$, in good agreement with its value $n=0.333$ for a sphere.

The magnetization curves were plotted at $4.2\ \mathrm{K}\leq T \leq T_c$. Examples, as $T\to T_c$, are shown in Fig. 1b. The higher noise level at $H>H_{c1}(1-n)$ is due to the temperature instability, and this limits the maximum measurement temperatures.

It should be noted that at high field sweep rates a dynamic hysteresis sets in, and the magnetic moment of the sample differs from the stationary value. There are no dynamic effects at all at a sweep rate $H_{c2}^{-1}dH/d\tau \leq 2$–$3\ \mathrm{h}^{-1}$. Accordingly, it took a half-hour to plot each magnetization curve.

The magnetization curves were used to determine H_{c2}, H_{c1}, H_{cm}, $dM'/dH|_{H=H_{c2}}$, H_2, and $M'(H_2)$. The field H_{c1} was determined from the intersection of the linear section of the descending part of $M'(H)$ and the straight line for the Meissner state (Fig. 1a): $H_{c1}=H_1/(1-n)$.

To reduce the measurement data we used the connection between the magnetization curves of a superconducting ellipsoid and of a long cylinder, obtained in Ref. 10: the distance between the points corresponding to identical values of the magnetic moment on the rising sections of the magnetization curves of a long cylinder and an ellipsoid is equal to the distance between the points at the same value of the moment on the descending sections.

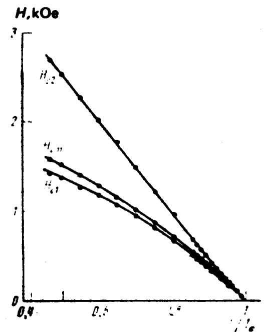

FIG. 2. Temperature dependences of the critical fields.

With allowance for this conclusion we obtain for the field H_2

$$B_0=H_2+4\pi M'(H_2)(1-n). \tag{3}$$

It follows from the same relation that

$$\frac{dM}{dH}=\frac{dM'/dH}{1-4\pi n\,dM'/dH}, \tag{4}$$

where M is the magnetic moment of the long cylinder, M' that of an ellipsoid with a demagnetization factor n; for the parameter $\varkappa_2$ we have

$$\varkappa_2=\frac{1}{\sqrt{2}}\left[1-\frac{n}{\beta}+\frac{1}{4\pi\beta}\left(\frac{dM'}{dH}\right)^{-1}_{H=H_{c2}}\right]^{1/2}. \tag{5}$$

As usual,

$$\varkappa_1=H_{c2}/\sqrt{2}\,H_{cm}. \tag{6}$$

We have assumed $\beta=1.1596$, which corresponds to a triangular vortex lattice.

3. RESULTS AND DISCUSSION

The temperature dependences of the critical fields are shown in Fig. 2. The results agree well with the known measurements of these parameters.[6,7] In the immediate vicinity of T_c, the critical fields have a linear temperature dependence (Fig. 3), and $T_c dH_{cm}/dT$

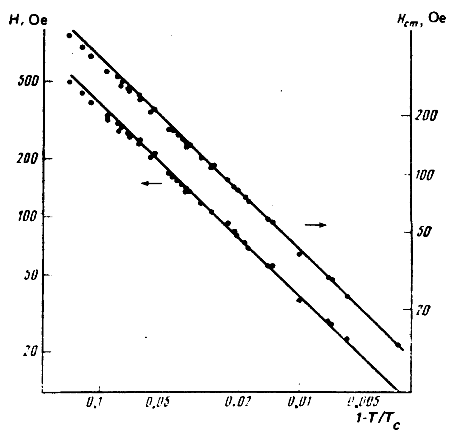

FIG. 3. Critical fields of niobium near T_c.

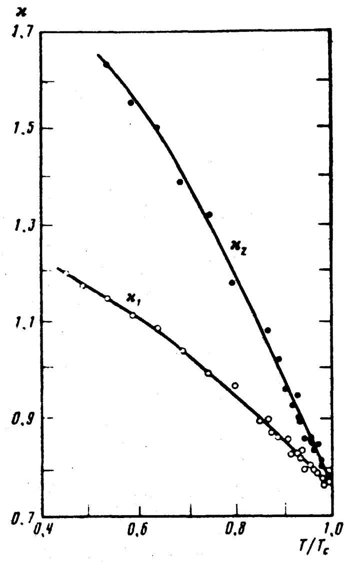

FIG. 4. Temperature dependences of $\varkappa_1$ and $\varkappa_2$ of niobium.

$=-4064$ Oe, which is practically the same as the result $T_c dH_{cm}/dT=-3986$ Oe of Ref. 11. Near T, the field H_{c1} is also linear in the temperature and $H_{c1}/H_{cm}=0.96 \pm 0.02$.

The temperature dependences of the parameters $\varkappa_1$ and $\varkappa_2$ are shown in Fig. 4. Near T_c we have

$$\varkappa_1=0.754+0.97(1-t)\pm 0.004, \tag{7}$$

$$\varkappa_2=0.756+2.26(1-t)\pm 0.004. \tag{8}$$

Niobium with a resistivity ratio $\rho_{300K}/\rho_{10K}=840$ is thus as $T\to T_c$ a type-II superconductor with $\varkappa_0=0.755$. The same result is deduced from the form of the magnetization curves as $T\to T_c$ (see Fig. 1b). Despite the near-linear plot of $M'(H)$ at $H>H_{c1}(1-n)$, its slope differs substantially from that corresponding to a type-I superconductor (dashed line in Fig. 1b). The ratio H_{c1}/H_{cm} was calculated within the framework of the Ginzburg-Landau theory in Refs. 12 and 13. For $\varkappa_0=0.755$ we find from Ref. 12 that $H_{c1}/H_{cm}=0.962$, while the results of Ref. 13 give $H_{c1}/H_{cm}=0.964$, agreeing within the limits of error with the value obtained in the present paper.

Starting from the value $\varkappa_0=0.755\pm 0.004$ and from the resistivity $\rho_{res}\approx 1.67\times 10^{-8}$ $\Omega\cdot$cm of our sample at the measurement temperatures, we can estimate the values of $\varkappa_0$ for ideally pure ($\rho_{res}=0$) niobium. We use for this purpose the known relation

$$\varkappa_0=\varkappa_{0\,pure}+A\rho\gamma^{1/2}, \tag{9}$$

where $\gamma=7.2\times 10$ erg/cm$^3\cdot$K^2 is the coefficient of the electronic part of the heat capacity and ρ is the resistivity. For a spherical Fermi surface $A=7.5\times 10^3$. Experiment yielded for niobium $A=8.1\times 10^3$, (8.0 to 12.2) $\times 10^3$, and 10.5×10^3 in Refs. 14, 2, and 6, respectively.

With A in the range from 7.5×10^3 to 12.2×10^3 we obtain $\varkappa_{0pure}=0.741-0.738$, i.e., at $T\to T_c$ absolutely pure niobium is a type-II superconductor, at variance with the result of Ref. 6. This difference is apparently attributable to the influence of the dynamic effects at the insufficiently slow field sweep in Ref. 6.

The temperature dependences of the parameters $\varkappa_1$ and $\varkappa_2$ as $t\to 1$ ($\varkappa_0^{-1}d\varkappa_1/dt=-1.28$, $\varkappa_0^{-1}d\varkappa_2/dt=-2.99$) are close to those obtained experimentally by others,[7,8] and differ greatly from the theoretical values obtained in the spherical-Fermi-surface approximation, namely $\varkappa_0^{-1}d\varkappa_1/dt=-0.41$ in Refs. 15 and 16 and $\varkappa_0^{-1}d\varkappa_2/dt=-0.91$. An estimate of $\varkappa_0^{-1}d\varkappa_2/dt$ was obtained by averaging the values of $\varkappa_2$ calculated by means of Eq. (5) from the magnetization curves calculated for $\varkappa_0=0.7$ and $\varkappa_0=0.8$ in Ref. 17.

The equilibrium induction B_0 was determined from Eq. (3), where H_2 and $M'(H_2)$ correspond to a point on the magnetization curve at which the dependence of the magnetic moment on the field deviates from the linear relation $M'=(H-H_{c1})/4\pi n$. The temperature dependence of B_0/H_{cm} is shown in Fig. 5. The dashed line shows the values of B_0/H_{cm} at $\varkappa_0=0.85$, determined from the results of the theoretical calculation (see Fig. 2 of Ref. 5) under the assumption that the temperature dependence of $\varkappa_1(t)/\varkappa_0$ at $\varkappa_0=0.85$ coincides with the one measured in the present study. We note that the data obtained in Ref. 7 for B_0 in the region $t<0.9$ agree well with our results. The decrease of B_0/H_{cm} observed above $t=0.9$ correlates with the theoretical conclusion that the equilibrium induction vanishes as $t\to 1$ in the case of superconductors with $\varkappa_0>2^{-1/2}$. Unfortunately, the residual irreversibility of the magnetization curve near $H_{c1}(1-n)$ does not permit an exact measurement of the temperature at which B_0 vanishes. The $H_{c1}(t)$ dependence (Fig. 3) has likewise no singularities whatever in the region where B_0 vanishes.

We arrive thus at the conclusion that at $t\to 1$ and $\varkappa_1=\varkappa_2$ the value of H_{c1}/H_{cm} corresponds to that calculated within the framework of the Ginzburg-Landau theory for our value of $\varkappa_0$. The temperature dependences of $\varkappa_1(t)$ and $\varkappa_2(t)$ are much more strongly pronounced then expected from the theoretical calculations. It seems that the discrepancy is due to the failure to take into account in the theory the real effects of the anisotropy of electron and phonon spectra. The temperature dependence of the equilibrium induction B_0 agrees with the calculated value obtained for $\varkappa_0>2^{-1/2}$. Absolutely

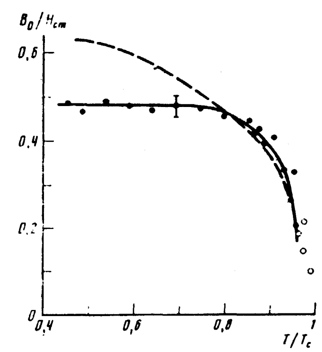

FIG. 5. Temperature dependence of the equilibrium induction B_0. Solid line—experiment, dashed—calculation. The light circle mean that the values of B_0/H_{cm} cannot be measured because of the residual irreversibility of the magnetization curve near $H_{c1}(n-1)$, but do not exceed the values shown in the plot.

pure niobium is a type-II superconductor at all temperatures $T \leq T_c$, with a parameter $\varkappa_0$ in the range 0.744–0.738.

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